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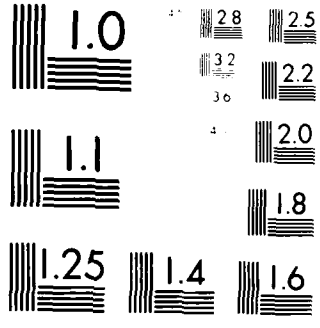

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INVESTIGATION OF THE EFFECT OF ANNEALING ON THE DISLOCATION AND SUB-GRAIN BOUNDARY CONTENT OF SOLVENT-EVAPORATION - GROWN CdTe

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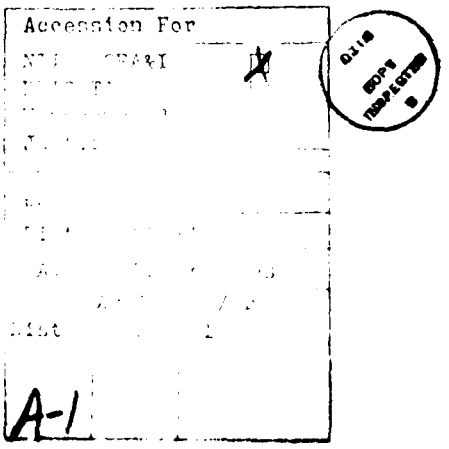
AUTHOR: N. Troughton

DATE: March 1984

SUMMARY

Solvent-evaporation grown CdTe wafers have been examined using optical microscopy and etching techniques to determine the subgrain boundary structure and density. The results indicate that the material contains subgrains of the order of 100-300 μm in diameter, the boundaries of which are formed by polygonised dislocations in densities exceeding 10^5 cm^{-1}. Annealing for periods of more than 24 hours at temperatures above 800°C leads to a reduction in the sub-grain boundary dislocation density and, in the best case, to complete removal of some of these boundaries.



INVESTIGATIONS OF THE EFFECT OF ANNEALING ON THE DISLOCATION AND SUB-GRAIN BOUNDARY CONTENT OF SOLVENT EVAPORATION GROWN CdTe

Nicholas Troughton

INTRODUCTION

Cadmium Telluride has theoretical potential to be a good material for device substrates. However, for best performance good quality single crystal material is essential. It is difficult to get large single crystals due to problems of growth - twinning [1] and other defects are easily grown into crystals. Epitaxial layers grown by MOCVD show up these faults as they can easily "grow through". Even if a large grain is chosen, the surface layer is still not good. This can be due to low angle grain boundaries or subgrain boundaries.

The examination of these sub-grain boundaries, and attempts to remove them from slices is the scope of this project. Three main techniques were used to examine the problem; etching, mechanical deformation of samples and annealing. Etching along with optical and infra red microscopy was used to find the effects of mechanical deformation and annealing.

ETCHING

Etching is a method commonly used in materials work to probe the structure of a material. The material is polished, mechanically and chemically to ensure a mirror polish. All the samples used were lapped with 60 μm carborundum and polished with 0.3 μm alumina/ethanediol, and finally chemically polished in 2% Br_2/MeOH. The etch will preferentially attack high energy areas and so readily shows up grain boundaries and twins. 2% Bromine-Methanol attacks the surface indiscriminately, as it reacts too fast to etch, and hence is used for a chemical polish.

Many etch mixtures have been used on cadmium Telluride [2] but the two most useful ones for sub-grain boundary examination are a weak bromine/methanol solution and a hydrogen peroxide/hydrofluoric acid solution.

The hydrofluoric/peroxide etch used is a 3:2:2 mixture of hydrofluoric acid: Hydrogen peroxide: water. The hydrofluoric acid used was 40%, Aristar grade, the hydrogen peroxide 100 vols Arialar, and the water was deionised. The samples were etched for ~ 30 secs, washed in water then methanol. To remove the inevitable black oxide film, a dip in dilute Bromine Methanol is essential. When the oxide film is removed to leave a shiny film; the sample is removed, washed in methanol and dried. The etch pits formed are easily visible under an optical microscope. Unfortunately, the etch will only attack the (111) A face of the crystal, so if the slice is not orientated correctly, it will not etch. The photograph (1) shows a grain which does have the right orientation, but has a large twin running through it, which is not affected by the etch. A dilute solution of Bromine-Methanol (about ½%) in the presence of light, will show up subgrain boundaries[2] This can be seen by the photograph (2). The photograph shows a grain boundary, three twins and a network of subgrain boundaries. The microscope has to be used with Nomarski interference attachment for maximum resolution of very small variations in surface topography. These variations are slight, and occasionally very difficult to see.

This makes them appear dubious evidence. They can be shown to be real effects rather than artifacts of bromine methanol light etching by repolishing and re-etching. This etching method is not as easy to achieve as the hydrofluoric acid-peroxide etch also used, but it is available on any orientation face.

INSTRON LOADING

The Instron is a machine to mechanically deform samples. It works by having a crossbar move downwards onto the sample. The crossbar is connected to a gearing arrangement to allow a variety of downward speeds. The sample is connected to a tension load cell which measures the load on the sample. A high load measurement shows that the sample can stand up to high stress. Cadmium telluride can not stand very large strain rates at room temperature. A small furnace can be fitted around the sample so as to heat the sample up. At ~ 200°C, Cadmium Telluride can be deformed plastically for 3% deformation at about 3×10^{-5} s^{-1} strain rate. After deformation, the sample has to be repolished, and etched to find out the defects put into the sample. (Fig 4)

ANNEALING

Annealing of samples was used to attempt to remove the defects. It is necessary to heat up the sample to high enough temperature to enable the defects to move in the sample. The annealing time has to be long enough for the defects to reach the edge. Then, once the defects are removed, the sample has to be lowered in temperature without fresh defects coming back in. Twins are very difficult to move grain boundaries move slowly, but nobody has attempted to study sub-grain boundary movement before.

Samples were placed in silica glass ampoules, with an excess of either cadmium or cadmium telluride and were pumped down to 10^{-7} torr. (The sample was normally left overnight even if this value is naturally achievable after a couple of hours). They were warmed to drive off any spare surface water when the vacuum was only about 10^{-4} torr. The samples were then sealed into a tube by heating the silica glass adjacent to the thimble until it melted, and caused a good seal. The sample tube was then put in the furnace, and left for varying periods of time. When the samples were removed, this could be done either slowly, allowing the sample to rest at an intermediate temperature, or dropped to room temperature. Sometimes the bulb was quenched to ensure that no cadmium could be deposited on the sample.

RESULTS

The Instron loading experiments failed to prove conclusively the removal or lack of removal of slip. This was due to

1) lack of sensitivity of etch towards slip bands

2) or lack of slip bands.

The lack of slip bands could have been due to the Instron load cell being entirely non functional. Sub-grain boundaries were neither moved on the surface or in the bulk.

Thin slices were annealed under the conditions laid out on the following table: the results column briefly relates how effective the annealing was. The CT 283 SE pieces did not possess a (111) A face so they could not be etched using the hydrofluoric etch which allows better definition. However, these pieces did not show subgrain boundaries clearing.

Sample	Temperature	XS Material	Length of anneal	Type of Cooling	Result
CT 283 SE 1	600	CdTe	6 hours	slow	No apparent removal of subgrain boundaries.
CT 283 SE 2	800	CdTe	18 hours	slow	Indistinct subgrains: Tellurium Precipitation.
CT 283 SE 3	600	CdTe	72 hours	slow	Indistinct etching result, but still subgrains.
CT 283 SE 4	600	CdTe	24 hours	fast	No apparent removal of subgrain boundaries.
CT 282 SE	600	CdTe	18 hours	fast	Inconclusive, some removal of structure?
CT 282 SE 21a	600	CdTe	24 hours	slow	No apparent removal of subgrain structure.
CT 282 SE 21b	600	CdTe	72 hours	fast	Some removal of the subgrain structure.
CT 282 SE 22a	600	CdTe	72 hours	slow	Better removal - but the overall result is still not good.
CT 282 SE 27	600	CdTe	168 hours	slow	Some areas show structure beginning to move.
CT 282 SE 19a	800	Cd	24 hours	fast	Some subgrain boundaries appear to have moved.
CT 282 SE 19b	800	Cd	96 hours	fast	Half of material reasonable.
CT 244 SE 15a	600	CdTe	168 hours	slow	Some subgrain boundaries appear to have moved, but not uniformly.
CT 244 SE 15b	800	Cd	48 hours	fast	Some subgrain boundaries have moved.
CT 244 SE 15c	800	Cd	96 hours	fast	Large clear patches, but still some areas of dense substructure.

DISCUSSION

The main parameters investigated were: length of anneal time, how rapidly the sample was cooled, and the temperature of the anneal.

Generally, the longer the sample was left annealing, the better the result. Sample CT 282 SE 21a was annealed for 24 hours (Photographs 5 & 6) whereas sample CT 282 SE 27 was annealed for 168 hours (Photographs 7 & 8). This shows the annealing is not completed at the shorter time, rather than the cooling is putting these faults back into the sample. For the high temperature annealing, the longer annealing times gave better results and for the 96 hour long annealing gave very good results in some areas of the sample.

Comparison of CT 282 SE 21b and 22a suggests that rapid cooling will put more stress into the samples and will give poorer results.

The higher temperature anneals generally gave better results. A short (24 hrs) anneal of CT 282 SE 19a gave a much better result than CT 282 SE 27 (compare photograph 9 & 10 with 5 & 6). Keeping the sample in even longer improved the surfaces. On CT 282 SE 19b half of the material exhibits strong subgrain structure whilst half seems 'clean' - see photographs 11 & 12. This suggests that the problem is not one of edges forming stresses in the cooling process, but incomplete removal of defects. Why the defects should be clustered on one side of sample is a mystery. They are not so clustered in the identically run sample CT 282 SE 15c; Photograph 13.

CONCLUSION

From this work I conclude that, it is possible to reduce the amount of subgrain boundaries in cadmium telluride by annealing at 800°C. Unfortunately, it may be difficult to anneal for the time necessary to do so without contaminating the sample. The subgrain structure may be further reduced by cooling the sample at a lower rate. This might be achieved by having a larger distance between the sample and the cadmium in the bulb of the ampoule when quenching.

REFERENCES

1. A. W. Vere, S. Cole, D. J. Williams,
   J. Electronic Materials Vol 12. No 3 May 1983

2. D. J. Williams - private communication

FIGURE CAPTIONS

Fig 1 CT 282SE/4 CdTe slice as grown

Fig 2 CT 282SE/4 (Normarski Contrast)

Fig 3 CT 282SE/4 Showing sub-grain structure

Fig 4 Slip lines introduced by plastic deformation in compression

Fig 5 CT 282SE/21a before annealing

Fig 6 CT 282SE/21a after annealing (24 hours at 600°C)

Fig 7 CT 282SE/27 before annealing

Fig 8 CT 282SE/27 after annealing (168 hours at 600°C)

Fig 9 CT 282SE/19a before annealing

Fig 10 CT 282SE/19a after annealing (24 hours at 800°C)

Fig 11 CT 282SE/19b after annealing (96 hours at 800°C). Specimen edge

Fig 12 CT 282SE/19b after annealing (96 hours at 800°C). Specimen centre

Fig 13 CT 282SE/15c after annealing (96 hours at 800°C)

Fig 1 CT 2823E/4 CdTe slice as grown

Fig 2 CT 2823E/4 (Normarski Contrast)

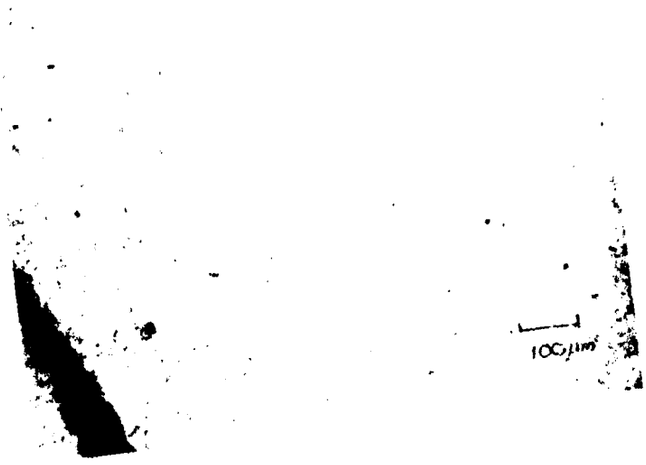


Fig 3 CI 282SE/4 Showing sub-grain structure

Fig 4 Slip lines introduced by plastic deformation in compression

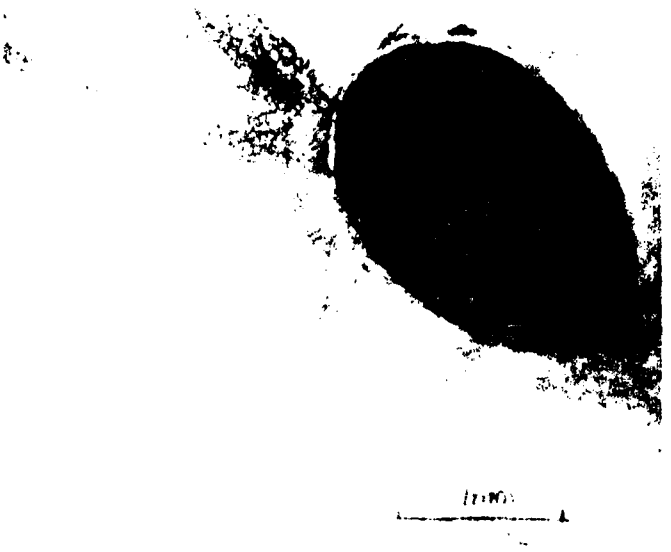


Fig 5 CF 282SE/21a before annealing

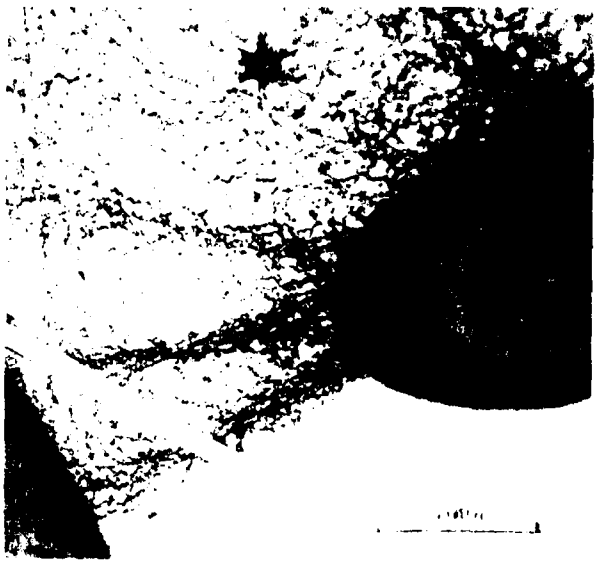


Fig 6 CF 282SE/21a after annealing (24 hours at 600°C)

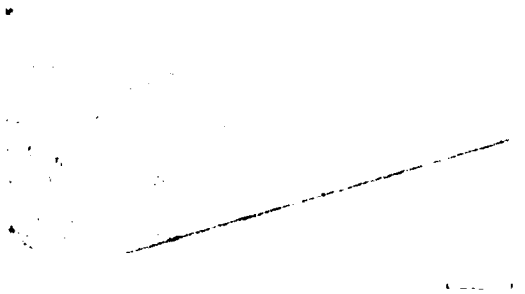


Fig 7 CT 282SE/27 before annealing 100μm

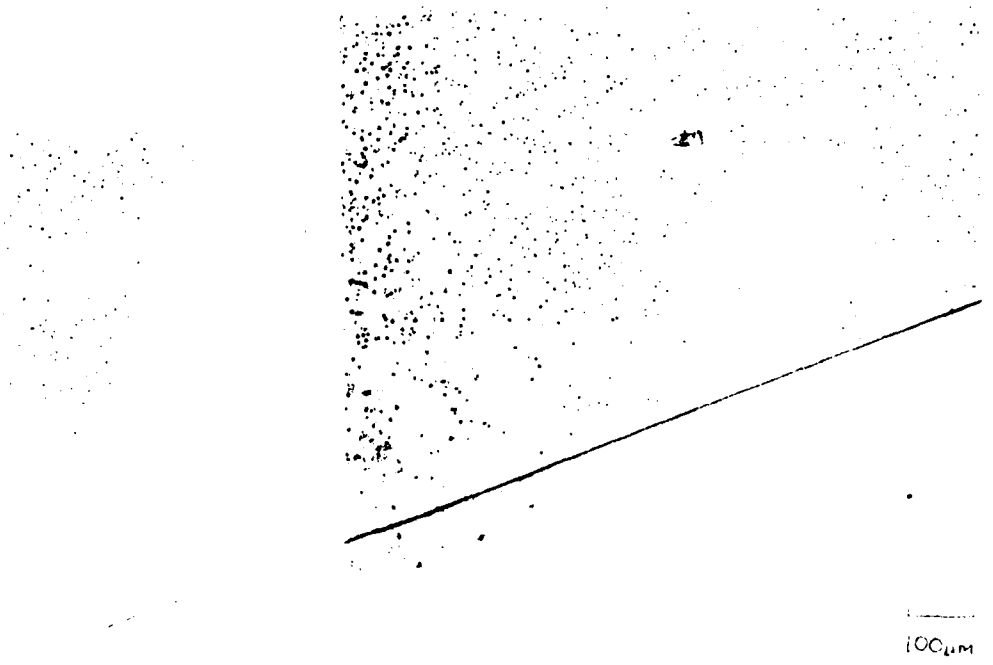


Fig 8 CT 282SE/27 after annealing (168 hours at 600°C)

Fig 9 CT 2825F/19a before annealing

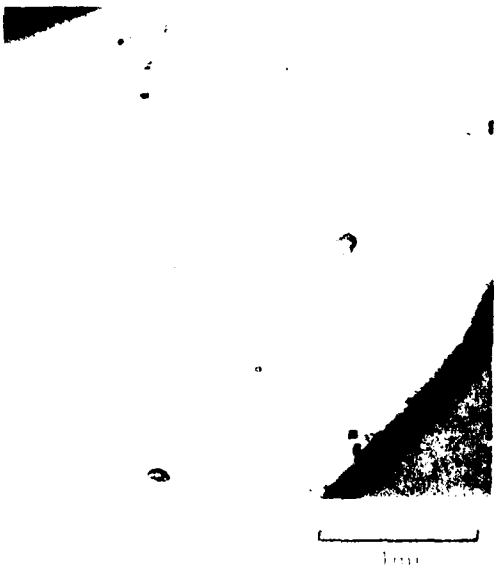
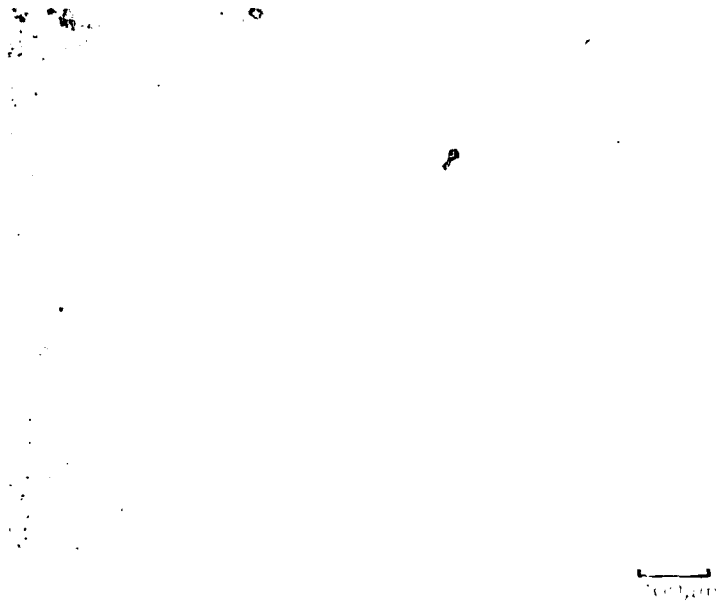


Fig 10 CT 2825F/19a after annealing (2 hours at 800°C)

Fig 11 CT 282SE/19b after annealing (96 hours at 800^{O}C). Specimen edge



12 CT 282SE/196 after annealing (96 hours at 800°C). Specimen centre

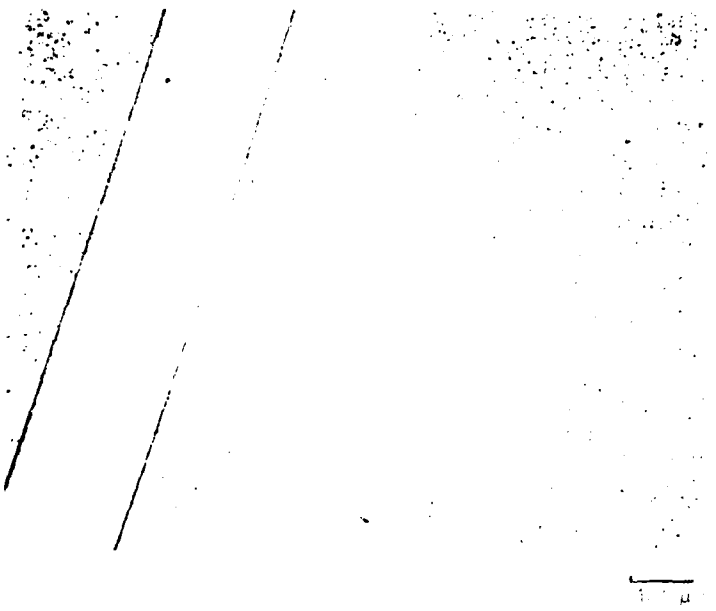


Fig 13 CT 282SE/1.. after annealing (96 hours at 800°C)

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